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# A kinetic model of zircon thermoluminescence

A.A. Turkin [a], H.J. van Es [b], D.I. Vainshtein [b], H.W. den Hartog [b,*]

[a] National Science Center, Kharkov Institute of Physics and Technology, 61108 Kharkov, Ukraine
[b] Solid State Physics Laboratory, University of Groningen, 4 Nijenborgh, NL-9747AG Groningen, The Netherlands

**Abstract**

A kinetic model of zircon thermoluminescence (TL) has been constructed to simulate the processes and stages relevant to thermoluminescent dating such as: filling of electron and hole traps during the excitation stage both for natural and laboratory irradiation; the time dependence of fading after laboratory irradiation; TL experiments both after laboratory and natural irradiation. The goal is to inspect qualitative behavior of the system and to unravel the processes and determine the parameters controlling TL phenomena of zircon. The input parameters of the model, such as types and concentrations of the TL centers and energy distributions of the hole and electron traps, were obtained by analyzing the experimental data on fading of the TL-emission spectra of samples from different locations. EPR data were used to establish the nature of the TL centers. Glow curves and 3D TL emission spectra are simulated and compared with the experimental data on time-dependent TL fading. Theoretical dating curves for combined natural plus laboratory irradiation have been calculated for as-irradiated, faded and preheated samples. 

*Keywords:* Zircon; Thermoluminescence; Fading; Dating

## 1. Introduction

Zircon represents an attractive mineral for dating by means of the thermoluminescence (TL) method. The important property of zircon is the presence of high concentrations of radioactive U and Th resulting in high internal irradiation doses and high TL yield [1]. Experimentally, zircon exhibits a TL signal with a rather complicated spectral distribution, as well as a complex fading behavior. To understand these peculiarities and to use zircon for dating purposes one needs a kinetic model of TL. We believe that computer simulation of the relevant processes related to TL will allow us to avoid pitfalls when developing TL dating protocols for zircon. In this report a set of rate equations describing the charge transfer between non-radiative and radiative traps is formulated.

## 2. The TL model

The TL model is based on well-known ideas concerning TL in materials (see for example [2,3]). Irradiation (from external or internal sources) generates free defects – electron and holes – in the electron system, which participate in the following processes: (i) trapping by luminescent centers

* Corresponding author. Tel.: +31-50-363-4178; fax: +31-50-363-4879.
*E-mail address:* h.w.den.hartog@phys.rug.nl (H.W. den Hartog).

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(LC); (ii) capture by non-radiative electron or hole trapping centers; (iii) mutual recombination; (iv) recombination with defects of opposite charge at trapping centers; (v) thermally stimulated eviction of electrons or holes from traps; (vi) retrapping of electron and holes in deeper traps. It is assumed that in each recombination act of an electron and a hole at a LC a photon is emitted. It is known that the main TL activators in zircon are Tb and Dy. According to recent EPR studies in our laboratory, in natural zircon samples $Tb^{3+}$ and $Dy^{3+}$ impurities are traps for holes [4]. The energy levels and possible transitions used in the model are shown in Fig. 1.We found that three types of LC, which trap holes, are sufficient to describe the fading experiments. In addition to $Dy^{3+}$ and $Tb^{3+}$ centers, background centers (Bgr) are introduced into the model in order to account for the broad emission TL intensity distributed over the spectral range from 300 to 500 nm at low temperatures (Fig. 5). Since the nature of the Bgr centers is uncertain, for the sake of simplicity below we assume that some kind(s) of hole-type TL centers produces this broadband TL signal. The other centers, denoted by $N$ and $M$, are assumed to be non-radiative and capture electrons or holes, respectively, during the excitation stage (irradiation) and release them during fading, annealing or TL heating. Below the rate equations, describing the charge transfer shown in Fig. 1, are presented.

Concentration of free electrons exited into the conduction band:

$$\frac{dn_c}{dt} = K + \sum_i v_i^e(T) n_i - A_N n_c \sum_i (N_i - n_i) - A_m n_c \sum_k m_k - a n_c m_v. \quad (1)$$

Concentration of free holes in the valence band:

$$\frac{dm_v}{dt} = K + \sum_k v_k^p(T) m_k - B_M m_v \sum_k (M_k - m_k) - B_n m_v \sum_i n_i - a n_c m_v. \quad (2)$$

Concentrations of occupied non-radiative electron trapping centers (levels $N_i$):

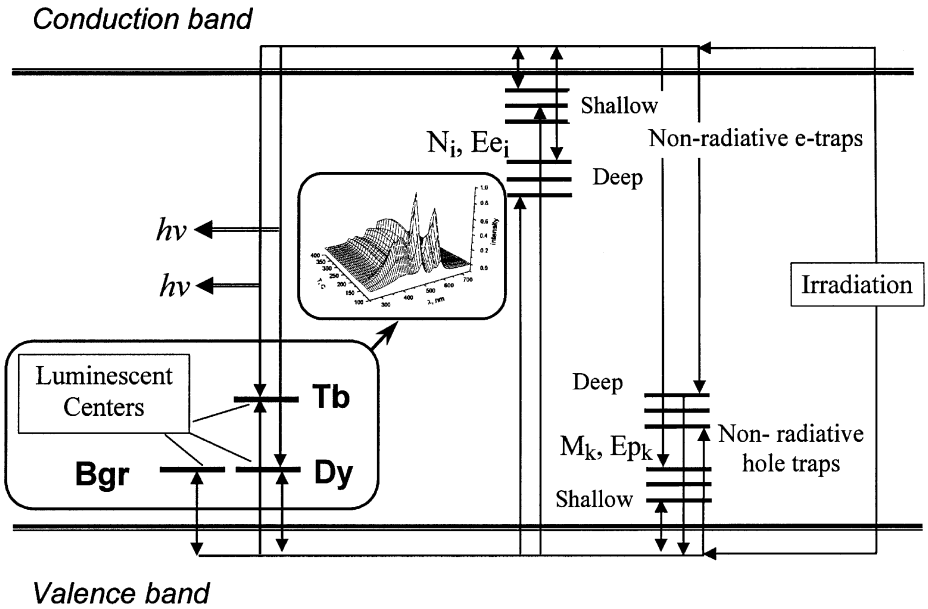


Fig. 1. A band diagram representation of the modeled electronic system. All allowed electronic transitions within the system are indicated by arrows. The Dy, Tb and Bgr are the only centers that produce a TL signal. $N_i$ is the concentration of electron traps with energy $Ee_i$, $M_k$ is the concentration of hole traps with energy $Ep_k$.

$$\frac{dn_i}{dt} = A_N n_c (N_i - n_i) - B_n m_v n_i - v_i^e(T) n_i, \quad i = 1, \ldots, ie. \tag{3}$$

Concentrations of occupied radiative (levels Dy, Tb and Bgr) and non-radiative hole trapping centers (levels $M_k$) are described by the equation similar to Eq. (3),

$$\frac{dm_k}{dt} = B_M m_v (M_k - m_k) - A_m n_c m_k - v_k^p(T) m_k, \quad k = 1, \ldots kp. \tag{4}$$

Here, the subscript $k$ refer to Tb ($k = 1$), Dy ($k = 2$), Bgr ($k = 3$) and non-radiative centers ($k = 4, \ldots, kp$). All concentrations are defined in terms of atomic fractions. The nomenclature is similar to that commonly used in the literature: $n$ and $m$ refer to electrons and holes, respectively. $v_i^e = s_e \exp(-Ee_i/k_B T)$ is the electron detrapping rate; $v_k^p = s_p \exp(-Ep_k/k_B T)$ is the hole detrapping rate; $s_{e,p}$ are the frequency factors for trapped electrons and holes, respectively; $K$ is the production rate of electron–hole pairs per lattice site (ionization rate). The rate coefficients for trapping and recombination, $\alpha$, $A_N$, $A_m$, $B_M$ and $B_n$, are assumed to be temperature independent.

The total luminescent intensity during the TL experiment, $I(t, \lambda)$, can be expressed in terms of: (i) the contributions from active LC, which are defined as the rate at which photons appear per lattice site i.e. as the recombination rate of electrons with holes trapped at corresponding LC:

$$I_{Tb}(t) = A_m n_c m_{Tb}, \quad I_{Dy}(t) = A_m n_c m_{Dy}, \quad I_{Bgr}(t) = A_m n_c m_{Bgr}, \tag{5}$$

and (ii) the spectral distributions of emitted photons, $\Phi_i(\lambda)$ ($i$ = Tb, Dy, Bgr),

$$I(t, \lambda) = I_{Tb}(t)\Phi_{Tb}(\lambda) + I_{Dy}(t)\Phi_{Dy}(\lambda) + I_{Bgr}(t)\Phi_{Bgr}(\lambda). \tag{6}$$

## 3. Results of numerical simulations

The set of material parameters used in the simulations are presented in Table 1 and Fig. 2. The parameters of the traps and LC were varied to obtain a good fit to the experimental data on TL fading in the samples from the Trail Ridge deposit (Florida, USA), which had been exposed to $\gamma$ irradiation [5]. To explain the difference in luminescent behavior of $Tb^{4+}$ and $Dy^{4+}$ it has been assumed that: (i) the $Tb^{3+}$ concentration is less than the $Dy^{3+}$ concentration, (ii) the binding energy of the holes with $Dy^{3+}$ ions is smaller than for $Tb^{3+}$ ions, i.e. $Dy^{3+}$ ions act as a shallow traps

Table 1
Material parameters

| | |
|---|---|
| Electron trapping coefficient, $\alpha$, $s^{-1}$ | $1.13 \times 10^{15}$ |
| Rate coefficients for trapping and recombination | $A_N = A_m = \alpha$<br>$B_M = B_n = 0.1\alpha$ |
| Electron attempt frequency for detrapping, $s_e$, $s^{-1}$ | $10^{14}$ |
| Hole attempt frequency for detrapping, $s_p$, $s^{-1}$ | $2.5 \times 10^{13}$ |
| Rate of production of free electron and holes under $\gamma$-irradiation, $K_{lab}$, $s^{-1}$ | $2 \times 10^{-10}$ |
| Rate of production of free electron and holes under natural conditions, $K_{Nat}$, $s^{-1}$ | $1.1 \times 10^{-17}$ |
| Time of laboratory irradiation, $t_{lab}$, days | 2.7 |
| Sample age, $t_{Nat}$, years | $10^4$ |
| Temperature of the sample during irradiation and fading, $T_0$, °C | 20 |
| Heating rate in TL experiment, $\beta$, $s^{-1}$ | 2.5 |
| Concentration of Tb, $M_1 = M_{Tb}$, ppm | 40 |
| Binding energy of hole with $Tb^{3+}$ ion, $E_{Tb}$, eV | >3 |
| Concentration of Dy, $M_2 = M_{Dy}$, ppm | 80 |
| Binding energy of a hole with a $Dy^{3+}$ ion, $E_{Dy}$, eV | 1.2 |
| Concentration of background LC, $M_3 = M_{Bgr}$, ppm | 90 |
| Binding energy of hole with background LC, $E_{Bgr}$, eV | 1.2 |

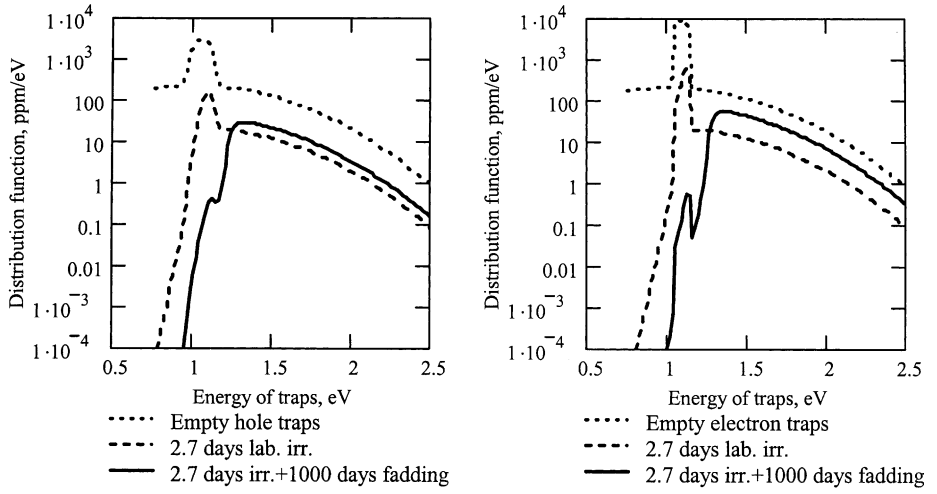


Fig. 2. Distribution functions of non-radiative hole (left) and electron (right) traps. Initial input distribution functions of empty traps are shown by dotted line. Dashed lines correspond to filled traps after 2.7 days of lab irradiation. Solid lines correspond to filled traps after 2.7 days of lab irradiation followed by $10^3$ days of fading (note the decrease of the fraction of occupied shallow traps and filling of the deep traps with $E \geqslant 1.5$ eV).

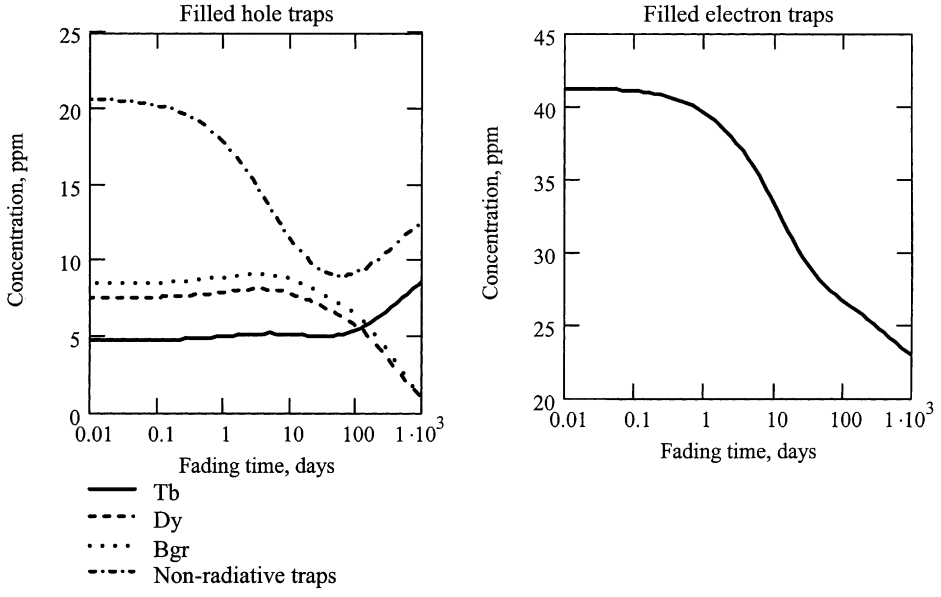


Fig. 3. Redistribution of the charge carriers over the traps during fading. The concentration of luminescent $Tb^{4+}$ centers increases at the expense of the holes released from the shallow traps, while the luminescent $Dy^{4+}$ centers decompose thermally.

for holes. The components of the emission spectra $\Phi_i(\lambda)$ have been deduced from the experimental data in [5,6] and then approximated by analytical expressions. The continuous distributions of the energy levels of the non-radiative electron and hole traps (Fig. 2) were replaced by discrete levels. The

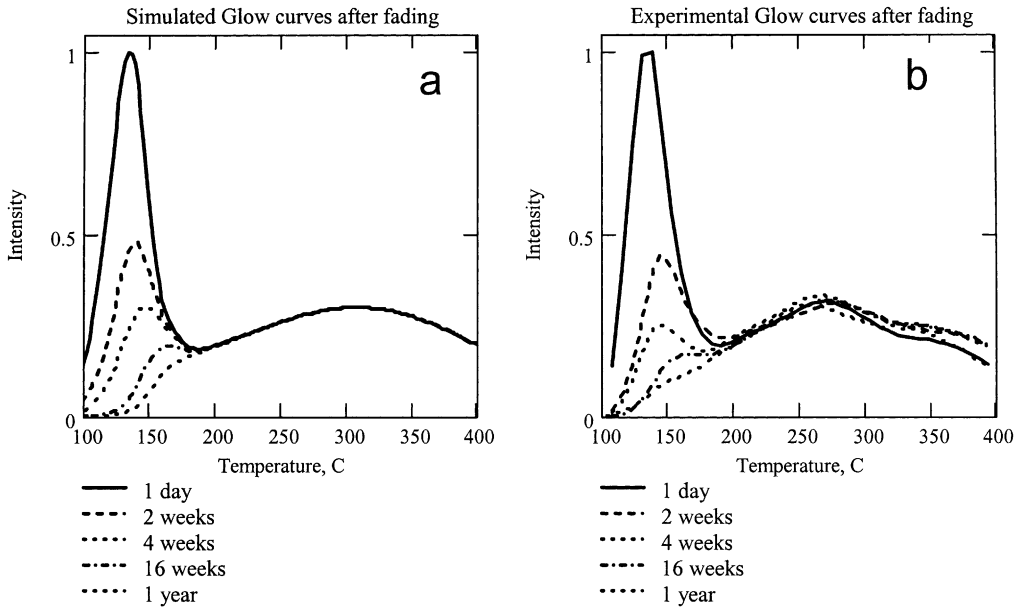


Fig. 4. Simulated (a) and experimental (b) glow curves after laboratory irradiation for different fading times. All data were normalized to the maximum intensity after 1 day fading.

resulting stiff set of about 200 ordinary differential equations was solved numerically.

Below we present the results of a simulation of a room-temperature *laboratory irradiation* of the annealed sample. The distribution function of occupied electron traps exhibits a peak (Fig. 2), which contributes to the luminescence at temperatures in the range from 100 to 200 °C. After the simulation of the laboratory irradiation the *fading process* during 1000 days was simulated. A considerable redistribution of electrons and holes between the traps is observed (Figs. 2 and 3). After the fading simulation the sample was investigated by modeling the *TL experiment.* Figs. 4 and 5 compare our simulation results with the real TL experimental data for the Trail Ridge samples.

The ultimate goal of our zircon studies is to develop a TL dating technique. It is not clear yet what treatment should be given to the sample after it has been exposed to the laboratory added dose in order to determine the equivalent dose [1]. There exists an opinion that prior to the dating measurements one should remove, by preheating, the $Dy^{4+}$ peaks, which are typical for laboratory irradiation. In Fig. 6 dating curves are presented for faded and preheated samples. During the simulations the samples were 'irradiated' with a natural dose rate for $10^4$ years, after this the sample was subjected to a laboratory 'irradiation' up to 19.2 h, which is equivalent to $4 \times 10^4$ years of natural irradiation (see Table 1). Then the TL signal was recorded immediately after the irradiation runs and after fading and preheating. It is seen that the post-irradiation treatment removes some part of the TL signal, which is a measure for the damage accumulated in the system during irradiation. Fig. 6 reveals that it might be possible to imitate the long-term natural irradiation by a combination of high dose rate laboratory irradiation plus a subsequent preheat at some moderate temperature. Detailed simulation studies might even lead to the conclusion, that reliable dating can be done on the basis of the luminescence properties of just the Tb-defects. For this purpose it is necessary to design special treatments (lab irradiation plus preheating or fading) with the help of computer simulations on the basis of the proposed multi-defect model.

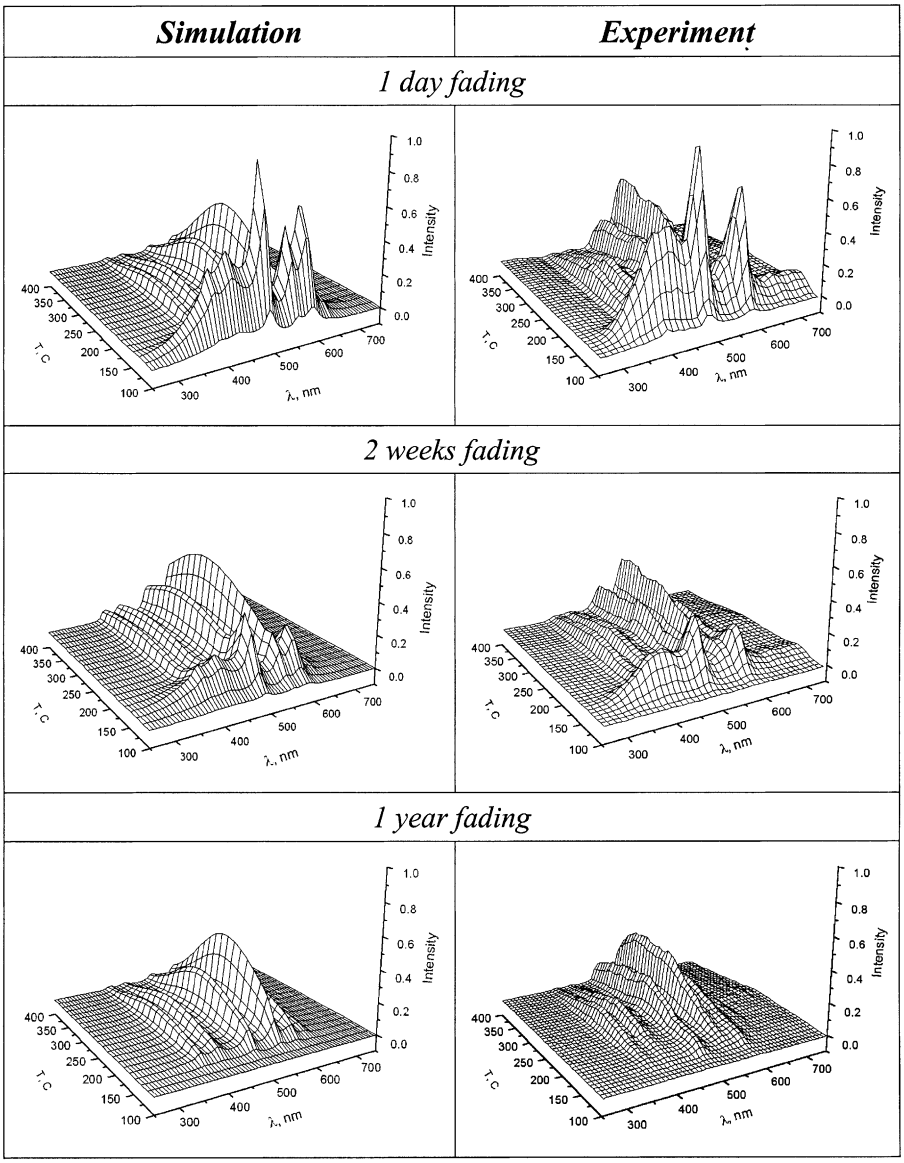


Fig. 5. Simulated and experimental 3D TL-emission spectra for the Trail Ridge samples [5] after laboratory irradiation.

## 4. Conclusions

- A model is presented for the description of the TL behavior of irradiated zircon.
- The main assumption of the model is that $Dy^{3+}$ ions are shallow traps for holes (as compared to $Tb^{3+}$ ions). The model requires rather high concentrations of shallow electron and hole traps to be able to explain the intense TL peaks due to $Dy^{4+}$ after laboratory irradiation.
- The material parameters used in this communication allow us to reproduce the experimental glow curves after laboratory irradiation followed by fading up to 2 years.
- The model can be used for the investigations of different scenarios for the dating procedure, in-

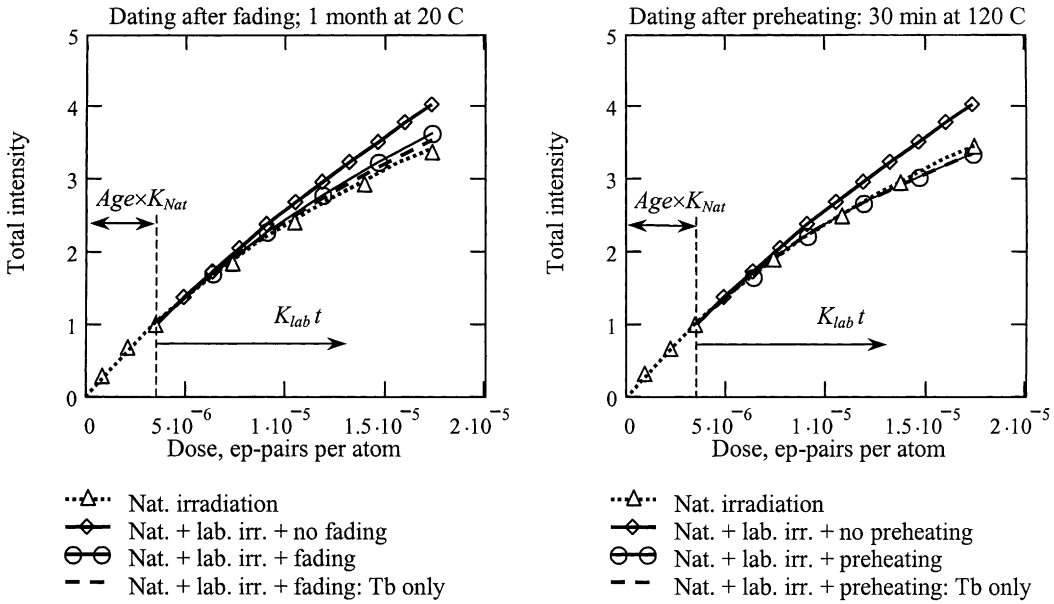


Fig. 6. Simulation of the procedure to determine the sample age. The total TL signals are normalized to the signal from the sample irradiated under natural conditions for $10^4$ years (corresponding dose $K_{Nat}t_{Nat}$).

cluding laboratory added irradiation, fading and preheat.

- Our results show that there exist excellent possibilities to develop an effective protocol to determine the equivalent dose, which is a necessary condition to carry out luminescence dating experiments using zircon as a working material.

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